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Lead Isotope Ratio Measurements for Source Identification Using Samples from the UK Heavy Metals Air Quality Monitoring Network

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Abstract: Lead isotope ratios vary depending on the origin of the lead, meaning that characteristic isotopic signatures can be used for source identification in environmental samples. Lead in ambient particulate matter was collected and analysed at 23 monitoring stations as part of the UK heavy metals air quality monitoring network to assess compliance with legislative limit values for allowable concentrations of lead in air. For the first time on a nationwide UK basis, isotopic analysis of lead was carried out on these samples to gain further information about the origin of the lead and the sources influencing measured concentrations at each of the monitoring stations. These measurements were undertaken with the novel application of ICP–MS/MS for high throughput analysis of over 200 samples from 23 sites across the UK. Values for 207Pb/206Pb ranged from 0.864 to 0.910 with an average standard error of 0.68%, while 208Pb/206Pb values ranged from 2.08 to 2.187 with an average standard error of 0.84%. The dataset was used to draw conclusions as to the main sources of pollution contributing to each site and has demonstrated the utility of ICP–MS/MS as a fit-for-purpose analytical method for the high throughput of a large number of samples in complex matrices. It was possible to identify different source types at the monitoring stations based on the lead isotope signature observed. Comparison with literature values showed clear links with traffic emissions at roadside sites and leaded petrol at a site near an airfield where small aircraft still use this type of fuel.

Keywords: ICP–MS/MS; lead; source identification; isotope ratio; air quality

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1. Introduction

Lead is a priority pollutant of interest, emitted by anthropogenic activities, including mining, smelting, fossil fuel combustion and incineration. Lead is primarily transported in the PM_{10} fraction of atmospheric particulate matter (particles with an aerodynamic diameter of 10 µm or less) [1]. Links have been seen between lead concentration in PM_{10} and lead concentration in the blood of local populations [2], suggesting inhalation and ingestion of these particles can be a significant route of exposure to humans. Studies have concluded that no detectable level of lead in blood is safe; effects include lowered mental proficiency, neurodevelopmental disorders, and damage to the central nervous system, heart, lungs and kidneys [3,4].

The most significant contributor to ambient lead concentrations historically was leaded petrol, the use of which peaked in the 1970s and 80s. The introduction of limits on lead content in petrol through the European Motor Fuel Regulations, introduction of unleaded petrol, and the subsequent ban of leaded petrol led to significant reductions in atmospheric lead from the late 1980s, as outlined in Figure 1 [5,6]. Despite this, ambient lead concentration is still significantly higher than pre-industrial levels [7] and higher than expected from emissions inventories [8]. Studies suggest that there may be unaccounted sources of lead contributing to this, including resuspension of historical lead deposited in soils [3]. Currently, lead in PM_{10} is regulated in the UK at 250 ng m^{-3} by the Air Quality Standards Regulations [9] and EU Air Quality Directive 2008/50/EC [10].

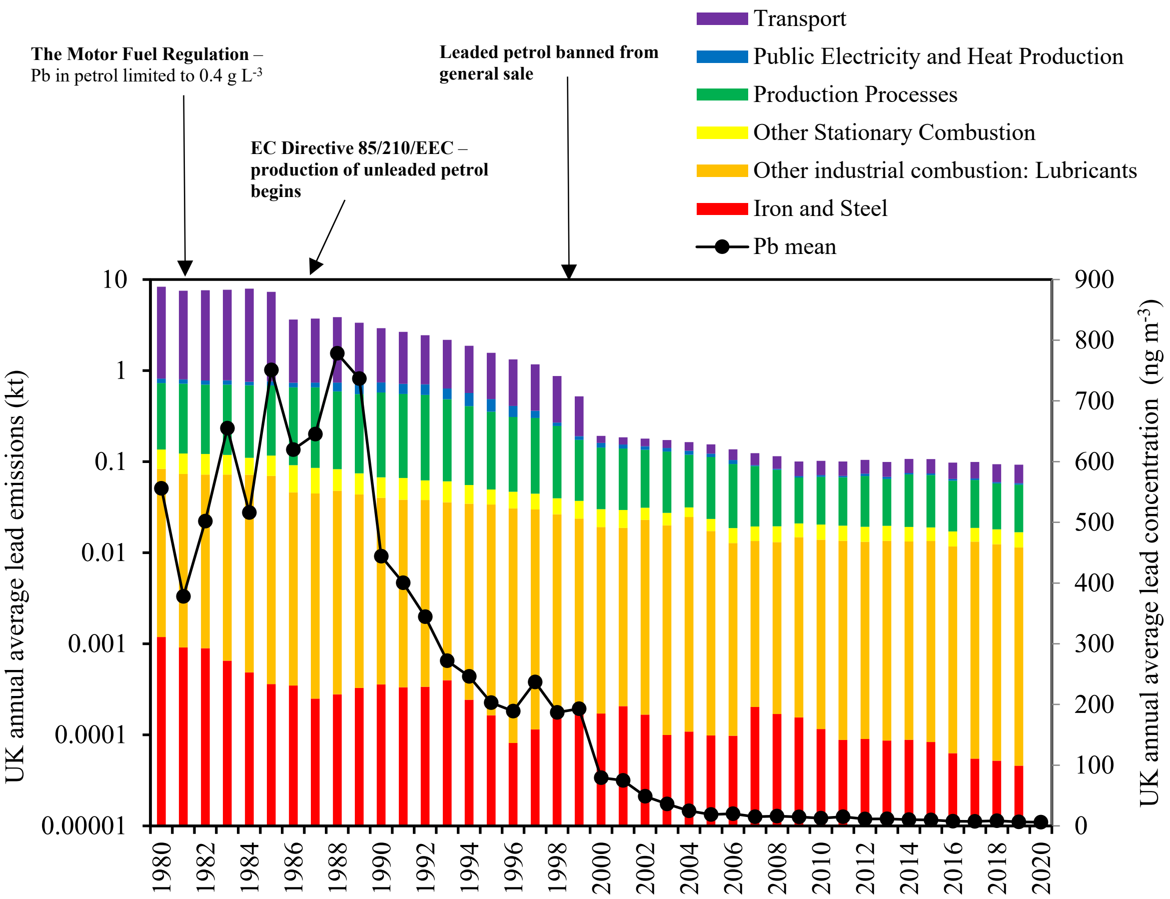

Figure 1. Lead emissions from the UK National Atmospheric Emissions Inventory (NAEI) and UK annual average concentrations measured by the UK Heavy Metals Monitoring Network, from 1980–2022.

In order to assess compliance with aforementioned limits, lead is measured in PM_{10} as part of the UK Heavy Metals Network, which is operated by the National Physical Laboratory (NPL) for the Environment Agency (EA) on behalf of the Department for Environment, Food and Rural Affairs (DEFRA). Its purpose is to assess compliance with legislation amounts of lead, nickel, arsenic and cadmium, assess long-term trends, determine the exposure of the public to these pollutants, and evaluate abatement and policy interventions. The network currently consists of 23 sites across the UK [6], with site locations chosen in accordance with the requirements established in the EU Air Quality Directives. The sites can be classified into five 'site environment types': rural background, urban background, urban traffic, urban industrial and suburban industrial [11]. These indicate the sort of processes that each site is likely to monitor. "Industrial" sites assess concentrations in high-density industrial process regions, whereas "traffic" sites evaluate concentrations close to busy roadways [12]. There are other categories of "urban" and "rural" sites. The former assesses concentrations from diffuse sources in built up areas, while the latter is situated in an area that is far from cities and towns, measuring background concentrations [6]. Site classifications may only be related to a few, or even to just one of the measured metals.

Although elemental concentration measurements carried out by the network are suitable for the assessment of compliance against legislation, to inform future policy and to identify sources, higher-resolution source identification is required in some areas where multiple factors are contributing, including wind and weather impacts. Isotope ratio measurements have been identified as a possible solution to this, which allow differentiation between natural and anthropogenic sources. The isotope ^{204}Pb (1.4%) is non-radiogenic, whereas ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{208}Pb (52.4%) originate from the naturally-occurring decay chains of ^{238}U, ^{235}U and ^{232}Th, respectively [13]. As a result of this, lead isotope composition varies in ore deposits depending on separation from source and formation condition, and therefore characteristic isotopic signatures can be used for source identification [14].

Studies have previously carried out lead isotope ratio measurements using multi-collector ICP–MS [3,4,15–17]. Work by Resongles et al. and Dong et al. applied this to ambient air quality measurements, with the former claiming a continued contribution of leaded petrol to ambient air [3,15]. The latter focusses on traffic emissions, and states that recycled petrol and road dust are major contributors to ambient lead concentrations. Studies using multi-collector ICP–MS reported precision of 0.005–0.1%, or larger for ratios that include ^{204}Pb [3,15,18]. Several studies have also used quadrupole ICP–MS for studies of ambient particulate matter; these studies reported a precision of 0.02–3% [18–21].

Usman et al. compared multi-collector ICP–MS with quadrupole setups for lead isotope ratio measurements. It was concluded that single quadrupole ICP–MS can provide valuable source identification information for most lead isotope ratios but that further efforts should focus on improving measurement of the ^{207}Pb/^{204}Pb ratio [22]. While measurement with ICP–MS/MS has lower signal-to-noise ratio and is not as precise as a multi-collector instrument, it allows for a more robust, high-throughput method with online interference removal. Reduced need for offline sample preparation makes the technique rapid and cost-effective and this is the optimum tool for such analysis, conducted routinely on a large number of samples from a nationwide air quality monitoring network such as this. Therefore, in this study, tandem ICP–MS is used to assess isotope ratios in PM_{10} samples from the UK Heavy Metals Network for the purpose of source identification—the first time this has been carried out on a UK nationwide basis using samples from an air quality monitoring network. This information will be used to assess the site type designations that have been applied as part of the UK Heavy Metals Network and inform future assignments and site placings.

2. Materials and Methods

2.1. Study Area

Metals analysis for the UK Monitoring Network involves sampling over one-week periods using Digitel DPA-14 samplers (Enviro Technology Services Ltd., Stroud, UK) with PM_{10} size selective heads on cellulose ester filters. Site names, types and abbreviations are summarized in Table 1 [23]. A map of the sites is shown in Figure 2. Over 200 digested samples from the UK Heavy Metals Monitoring Networks were used in this study, from November 2021 to November 2022. As the samples were spread evenly throughout the year, and lead seasonality has been shown elsewhere to be insignificant [24], seasonality should have had minimal effect.

2.2. Method for Elemental Lead Analysis

Sampled filters undergo a microwave acid digestion using an Anton Paar 5000 with a combination of HNO_3 and H_2O_2. Analysis for lead, and other elements not discussed in this study, is undertaken by 8800 and 8900 tandem inductively coupled plasma mass spectrometry (ICP–MS/MS) (Agilent, Santa Clara, CA, USA), equipped with two quadrupole mass filters separated by a collision–reaction cell. The instruments were fitted with standard sample introduction systems including a MicroMist nebulizer and quartz double-pass spray chamber. Platinum sample and skimmer cones were used with a plasma gas flow rate of 15 L min^{-1}. The analysis method follows BS EN 14902:2005 and is fully traceable to the SI through calibration against NIST SRM 3136, 3103a, 3108 and 3128 standard solutions for nickel, arsenic, cadmium and lead [25,26]. The digestion and analysis is validated with NIST SRM 1468a (urban particulate matter) and NIES CRM No. 28 (urban aerosols). Quality assurance and control checks are undertaken in each digestion and analysis, including spiked filters and analysis solutions. More information on the network can be found on the Defra UK Air website, where data is publicly available [27], and long-term trends are discussed in depth elsewhere [5,6].

2.3. Method for Lead Isotope Ratio Analysis

An 8900 ICP–MS/MS (Agilent, Santa Clara, CA, USA) was used, with the same instrument setup as mentioned above. Thallium (Tl, m/z = 205) was employed as an internal standard, introduced through a mixing block, for drift monitoring, since it is of similar mass to lead isotopes without any isobaric interference [28]. A 0.1 g portion of NIST SRM981 lead wire was digested to produce a set of calibration standards of mass fraction 5, 10, 15, 20 and 30 ng/g.

Table 1. Identifiers, names, abbreviations and types of sites in the UK Heavy Metals Network.

Site ID	Site Name	Abbreviation	Site Type
62	London Westminster Horseferry Road	HRd	Urban background
65	Eskdalemuir	Esk	Rural background
100	Swansea Coedgwilym Cemetery	SwCo	Urban background
101	Swansea Morriston Groundhog	SwMo	Urban traffic
103	Belfast Centre	BC	Urban background
104	Port Talbot Margam	PT	Urban industrial
106	Scunthorpe Town	ScTo	Urban industrial
107	Scunthorpe Low Santon	ScLS	Urban industrial
110	Chadwell St Mary	CSM	Urban background
113	Pontardawe Tawe Terrace	PTT	Urban industrial
114	London Marylebone Road	LMR	Urban traffic
115	Pontardawe Brecon Road	PBR	Suburban industrial
117	Sheffield Tinsley	STin	Urban industrial
119	Sheffield Devonshire Green	SDG	Urban background
202	Auchencorth Moss	AMoss	Rural background
203	Yarner Wood	YW	Rural background
204	Cwmystwyth	Cwth	Rural background
206	Heigham Holmes	HH	Rural background
208	Detling	Det	Rural background
209	Fenny Compton	FC	Rural background
210	Chesterfield Loundsley Green	Chfd	Urban background
211	Chilbolton Observatory	Chilb	Rural background
213	Walsall Pleck Park	WPP	Urban background

Figure 2. Map of PM_{10} monitoring sites making up the UK Heavy Metals Monitoring Network [23]. Site abbreviations found in Table 1.

Measurements were performed in no gas mode at m/z = 204, 205, 206, 207 and 208. Initial assessment showed that due to the low abundance of ^{204}Pb, measurement sensitivity was poorest for this isotope, giving inferior repeatability between measurements. Therefore ^{206}Pb, ^{207}Pb and ^{208}Pb were favored for source identification analysis, as is often found in similar studies in the literature. Interference from Hg was assessed by monitoring m/z = 199, 200, 201, 202 and 204 on a subset of samples. The percentage contribution from Hg was calculated to be less than the percentage uncertainty of the total signal at m/z = 204 and therefore was deemed negligible. The number of sweeps per scan (3, 5, 10, 15, 20) and replicates (3, 5, 8, 10, 15) were also assessed. Optimal values of 15 sweeps and 5 replicates were chosen to minimize standard deviations while maximizing time efficiency by taking account of the large volume of samples used for the analysis. Dwell times of 0.1 ms were used for each mass. This resulted in an acquisition time of around 3.5 min per sample, which included sample uptake and a post-analysis rinse cycle.

Approximately ten samples from each site in the UK Heavy Metals Network were selected for measurement using the validated method. Data were calibrated against isotope concentrations in the NIST SRM981 lead wire, providing validation and traceability to the International System of Units. Calibration was performed using XLGenline version

2, NPL-developed polynomial fitting software [29]. To ensure detector consistency, some samples were diluted to ensure that all measurements were made with the detector in pulse mode. Uncertainties of total lead concentration as calculated for the network are 10–16% ($k = 2$, including uncertainties accumulated from the sampling process). Standard errors associated with the isotope ratio measurements are 0.5–2% and are the dominant contribution to the overall uncertainty in these measurements.

3. Results and Discussion

A summary of results for each site, including averages and uncertainties for elemental lead and isotopic ratios, can be found in Table 2.

Table 2. Site average lead concentration and isotope ratios.

Site ID	Average Lead Concentration (ng m^{-3})	Lead Concentration Uncertainty ($k = 2$)	Average ^{207}Pb/^{206}Pb	^{207}Pb/^{206}Pb Standard Error	Average ^{208}Pb/^{206}Pb	^{208}Pb/^{206}Pb Standard Error
62	4.4	0.5	0.880	0.002	2.105	0.006
65	0.7	0.1	0.876	0.004	2.150	0.015
100	11	1	0.897	0.014	2.181	0.030
101	9.4	1.3	0.890	0.010	2.112	0.030
103	2.2	0.3	0.876	0.004	2.124	0.015
104	6.9	0.8	0.865	0.010	2.091	0.026
106	13	2	0.875	0.012	2.125	0.021
107	18	2	0.864	0.005	2.100	0.018
110	6.9	0.8	0.901	0.007	2.145	0.015
113	5.8	0.7	0.870	0.005	2.128	0.011
114	5.0	0.6	0.887	0.005	2.083	0.037
115	6.3	0.8	0.909	0.011	2.187	0.029
117	15	2	0.876	0.003	2.130	0.011
119	5.5	0.7	0.871	0.003	2.114	0.011
202	1.0	0.1	0.879	0.005	2.113	0.007
203	1.2	0.1	0.880	0.002	2.141	0.010
204	1.6	0.2	0.874	0.008	2.113	0.018
206	2.4	0.3	0.880	0.004	2.113	0.007
208	4.3	0.5	0.888	0.006	2.136	0.011
209	2.7	0.3	0.877	0.004	2.090	0.011
210	5.2	0.7	0.887	0.003	2.080	0.036
211	2.6	0.3	0.910	0.009	2.179	0.026
213	6.2	0.8	0.882	0.003	2.122	0.008

3.1. Total Lead Concentration

All measurements of elemental lead were below the limit value of 500 ng/m^3 outlined in the UK Air Quality Standards Regulations [9]. It is noted that higher average total lead concentrations are generally observed at urban industrial sites (Figure 3) [26]. Unsurprisingly, rural background sites have the lowest concentrations. The same is true generally when considering individual samples, although there are some exceptions, e.g., the highest total lead concentration in the samples analysed was for Swansea Coedgwilym, which is categorized as urban background. The sites in this area target nickel emissions from the local industrial sites, but it can be assumed that higher metals emissions in general are likely to lead to high lead emissions. The Swansea Coedgwilym Cemetery site is generally downwind from Vale's Clydach Nickel Refinery (although there are very few ground level fugitive emissions, as these are highly toxic), but upwind from Wall Colmonoy metal alloy production plant. Emissions at Wall Colmonoy are released at roof level as opposed to via a high chimney stack, resulting in closer proximity to the monitoring station, and may be the reason for higher concentrations when the wind is not from the prevailing direction. The high lead concentration may be due to a one-off emission from the nearby industrial sites.

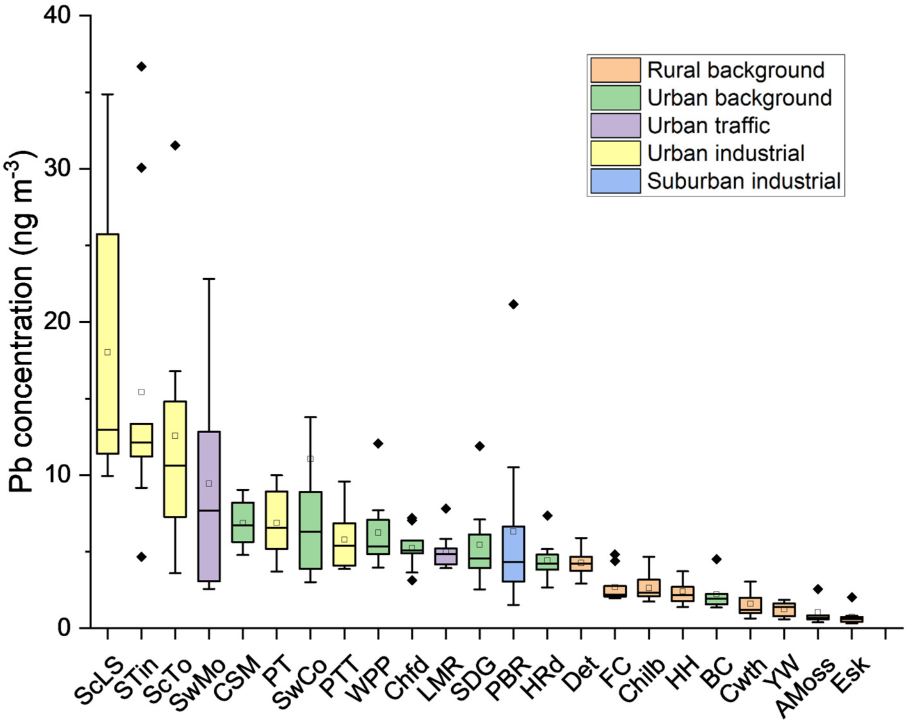

Figure 3. Total lead concentration at all sites plotted in Origin, with the site categorization shown by the colours of the bar. Site abbreviations can be found in Table 1. With the exception of the Belfast Centre, which is Urban background, all the sites to the right of, and including, Detling are Rural background. The boxes represent 25–75th percentiles of the data, while the whiskers show 1.5× interquartile range. The median is represented by the horizontal black line, the mean by the unshaded square and outliers by a solid black diamond. The maximum outlier for SwCo is at 54 ng m^{-3} and has been excluded from the plot for visual purposes.

It is important to note that the sites considered in this study are not all related to point sources of emissions and will in any case have multiple source contributions, varying dependent on wind direction, to the samples collected at each site. For this reason, the site categories are only indicative of the nature of the site, often based on only the one metal expected to have the most significant concentration, and so full source identification is often challenging. As an example, the monitoring stations in the Tawe Valley mentioned above are designated (sub)urban industrial because of the expected elevated concentration of nickel that they measure from local point sources, but for other metals they would be considered as urban background because of the emissions sampled from local diffuse sources, such as traffic and domestic and commercial heating. In this way, the site types may not relate if just lead was being considered, since none of the site types are allocated considering lead concentrations specifically.

3.2. Lead Isotope Ratios

The ranges of isotope ratios measured in this study, 2.080 to 2.187 for ^{208}Pb/^{206}Pb and 0.864 to 0.910 for ^{207}Pb/^{206}Pb, were in good agreement with other literature values for airborne particulate matter, as shown Figure 4. Precision was comparable to that of other studies using quadrupole ICP–MS, at 0.2 to 1.8%; typical standard errors were approximately 1%.

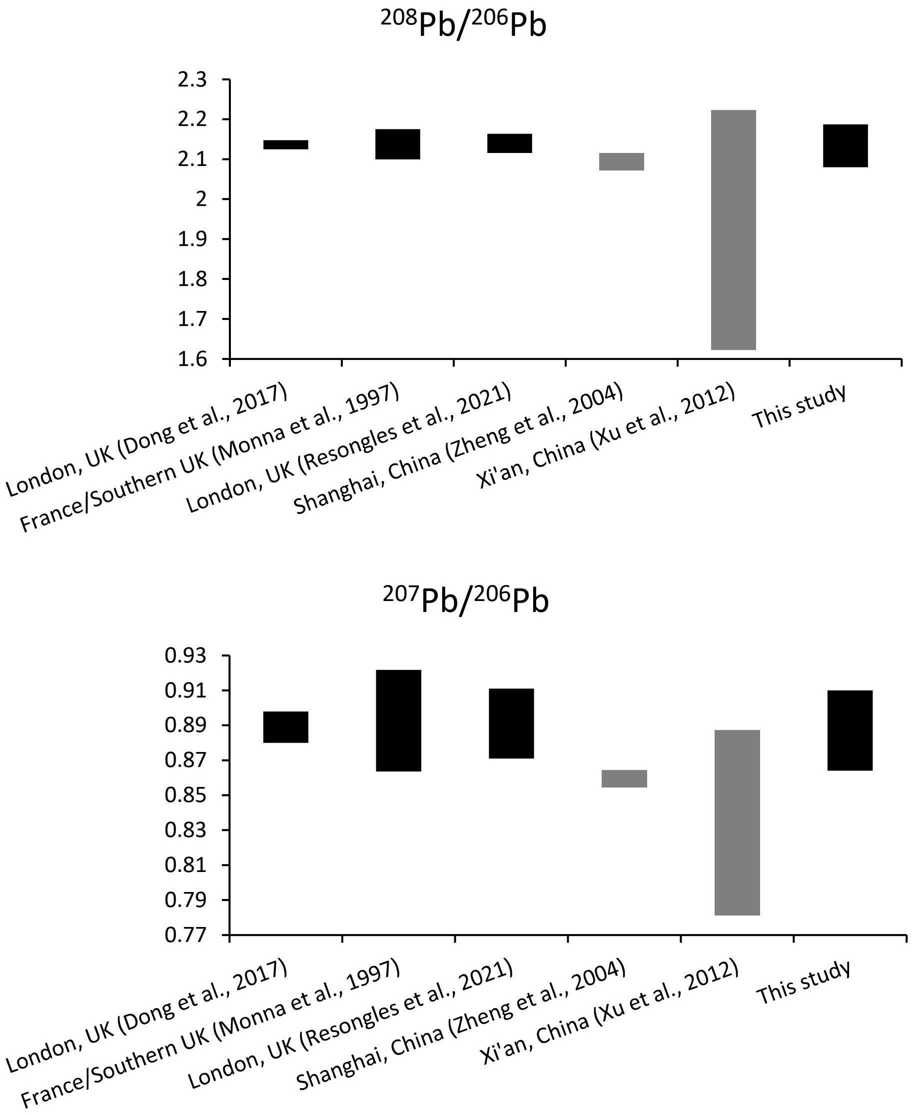

Figure 4. Ranges of isotopic ratios measured in other studies, where grey bars represent measurements made using quadrupole ICP–MS and black bars represent measurements made with other types of ICP–MS [3,13,15,19,21].

Site averages were taken for lead isotope ratios, which were plotted as ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb (Figure 5). Data points are clustered by site type, and in several cases clear separation can be seen between the different site types, indicating that the impact of lead emissions on these sites is broadly of the same character as the emission of the other metals on which the site type classification is based. Although there is some overlap between site types, which acts as a reminder that these sites receive contributions from a combination of sources, many data points have a significant statistical difference at the 95% confidence level. However, there are several outliers from the groups (as labelled in the plot), which are likely to indicate contributions for lead from other sources of significance, which are affecting isotope composition in a different way and are not consistent with the generic site type attributed to the site. Averages for each site type have been compared with values in the literature in Figure 6, and each of the outlying points are summarized in Table 3. The discrepancies between individual sites and their site types highlights that the current site types relate narrowly to regulatory requirements; it would be beneficial for the understanding of emissions protection and human health to give a site type for each element.

Table 3. Description of site outliers from type clusters.

Site	Classification	Rationale
Chadwell St Mary (CSM)	Urban background	Contribution from Britannia Metals, Tilbury docks and a power station located nearby.
Pontardawe Brecon Road (PBR)	Suburban industrial	Upwind from Wall Colmonoy nickel refinery 75% of the time so, whilst overall concentrations are relatively low, those that are measured are predominantly from industrial sources.
Swansea Coedgwilym (SwCo)	Urban background	Downwind from Vale nickel refinery but upwind from Wall Colmonoy refinery 75% of the time. Emissions from Wall Colmonoy are released at roof level as opposed to via a high chimney stack.
Chilbolton Observatory (Chilb)	Rural background	Chilbolton Flying Club and Airfield located nearby. Some small aircraft still use leaded petrol [31].
Chesterfield (Chfd)	Urban background	Suggested traffic contributions from Pennine Road (15 m to the south), the B6150 (450 m to the North) or Ashgate Road (490 m to the west).

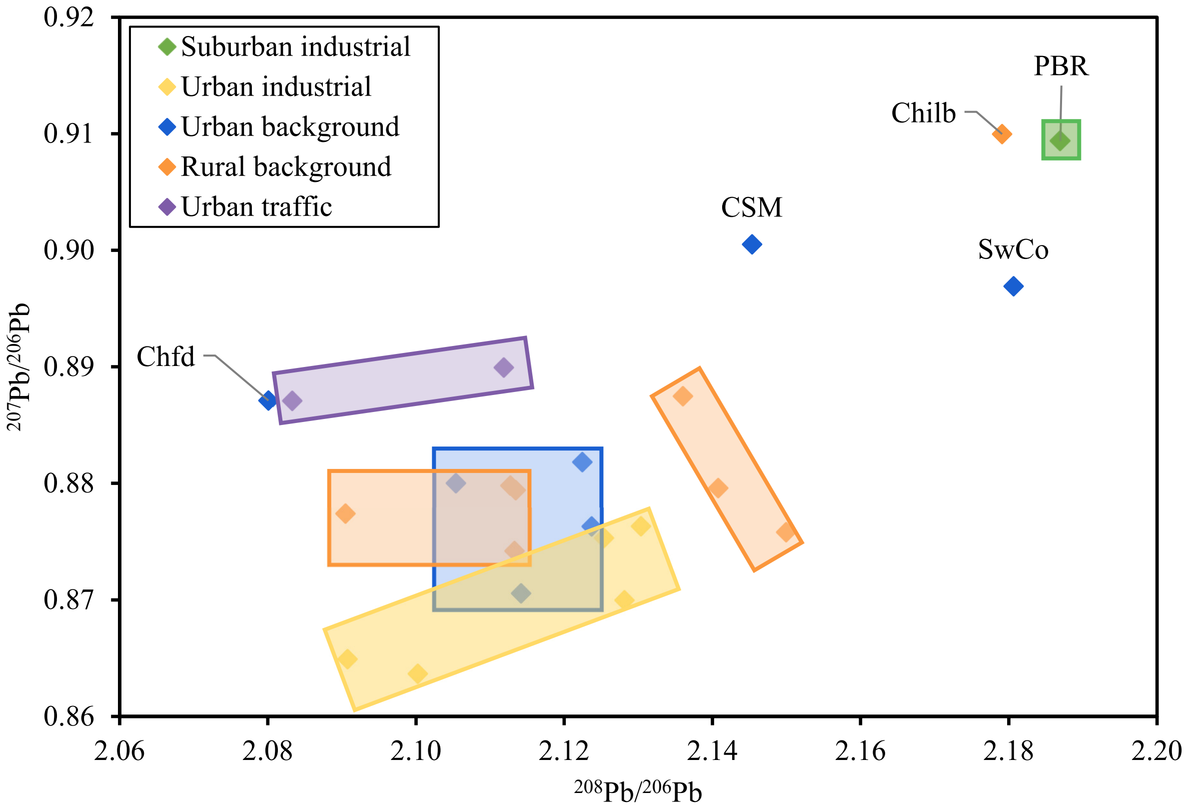

Figure 5. Site averages for ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb with the categorization by site type displayed, plotted in Microsoft Excel. Groupings are indicated by colored rectangles, which are for visual purposes only and do not have a statistical basis.

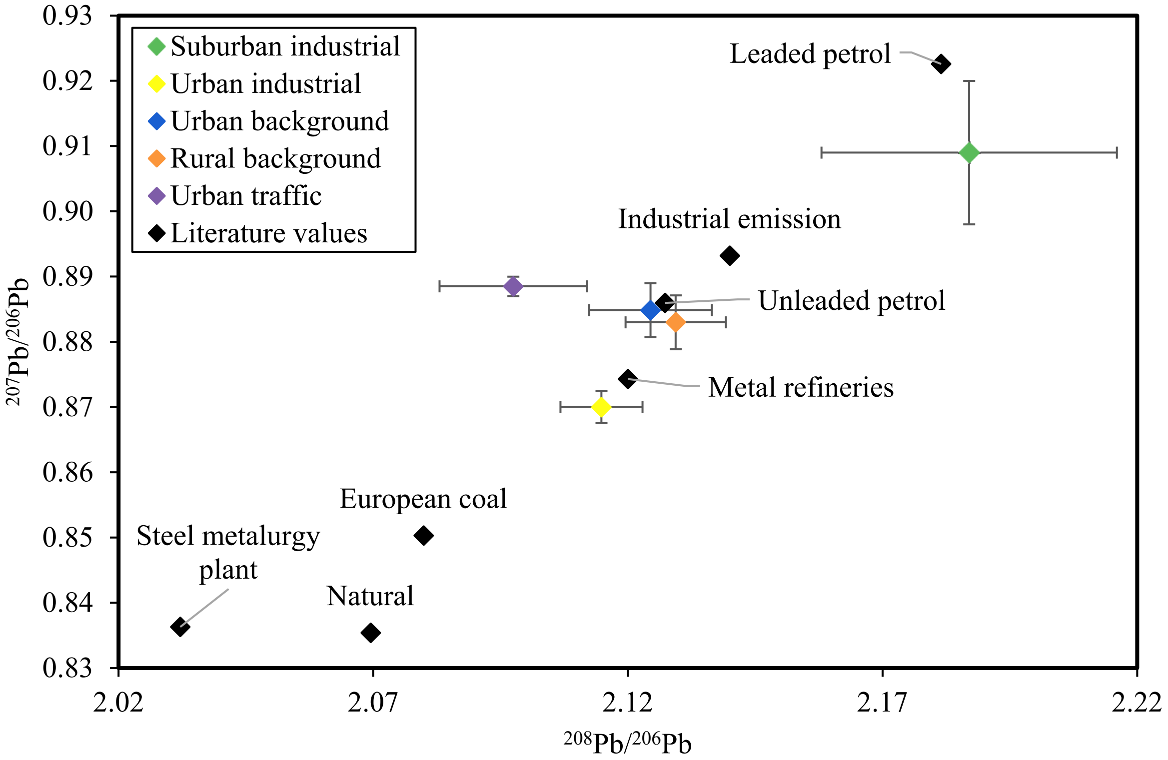

Figure 6. Site type averages for ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb, including literature values plotted in Microsoft Excel [30]. Error bars represent the standard error for each average. Differences can be seen between some site types up to the 95% confidence level.

3.2.1. Pontardawe Brecon Road and Swansea Coedgwilym

It is worth noting that both Pontardawe Brecon Road and Swansea Coedgwilym sites, both of which are outliers, are located in the Tawe Valley, within which the wind comes from the south-west approximately 75% of the time and from the north-east approximately 25% of the time. That means that, although the sites are placed upwind or downwind from industrial sources, the wind direction is not consistent and therefore contributions to the sites will vary depending on the wind direction. In addition to this, the valley funnels any local emissions, resulting in a higher chance of them reaching the monitoring stations instead of dissipating into the wider area. This results in the variation in isotope ratio from what is expected of their respective site types.

3.2.2. Chilbolton Observatory

Additionally, Chilbolton Observatory is a significant outlier as a rural background site. It is possible that this is due to contributions from the nearby flying club and airfield, even though contributions from such sources are stated in the NAEI to be very low but, since the overall concentrations measured at this site are also very low, even these small contributions would have a large effect on the isotope ratio observed [8]. As seen in Figure 7, each of these locations is within a 5 km radius of the monitoring station. Despite the ban on leaded petrol and universal acceptance of the metal's toxicity, lead is added to aviation gasoline to prevent engine knocking and lubricate engine components for Piston Engine Aircrafts [31]. Although elemental lead concentrations at Chilbolton are relatively low (see Figure 3), as expected for a rural background site, it seems that the contributions measured are different from other rural background sites and are in reasonable agreement with literature values for leaded petrol (see Figure 6). It may be the case that historic lead from small aircraft is being resuspended from the soil.

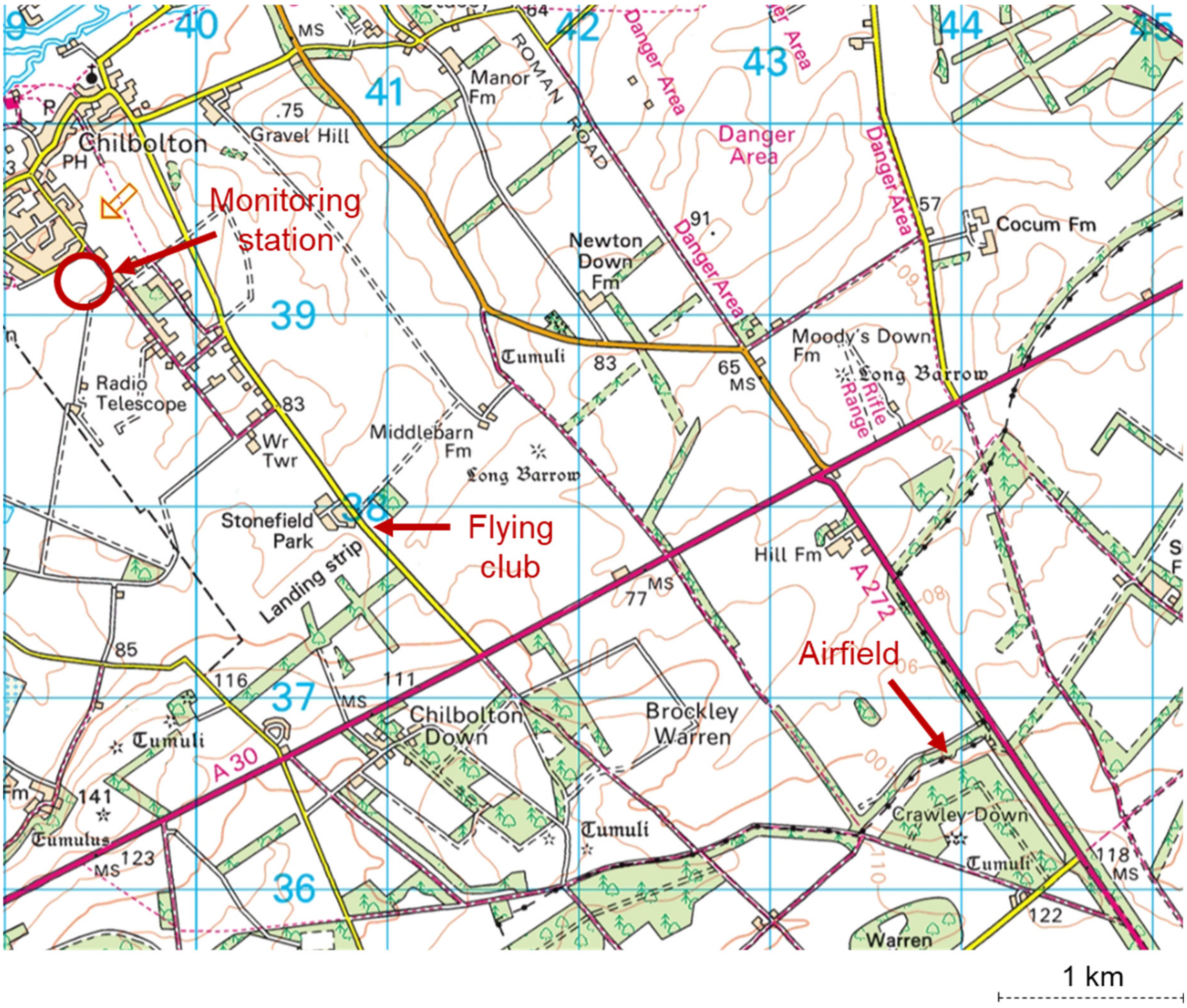

Figure 7. Map of Chilbolton with monitoring station, flying club and airfield labelled. For scale, the distance between the airfield and the shooting range is approximately 2.2 km.© Crown copyright and database rights 2024 licensed under DSIT's Public Sector Mapping Agreement with Ordnance Survey (license No. 100037028) and Defra's Public Sector Mapping Agreement with Ordnance Survey (license No. 100022861).

3.2.3. Literature Values

All sites fall within the extremes of the literature values for various sources, suggesting that there is a balance of all of these sources, but mostly influenced by industrial emissions and metal refining. Even in urban areas, the dominant contributions to lead concentrations are likely to be from the nearest metal refining plant. The literature values for emissions from metal refineries fall within the urban industrial/urban background/rural background regions, suggesting that refineries are the primary contributors to such sites. The difference must be noted between metal refineries and alloy production. The literature value for industrial emissions in airborne particulate matter fall between the values for Chadwell St Mary and Swansea Coedgwilym (both heavily affected by nearby industrial sites) and the urban industrial/urban background/rural background categories. The literature value for leaded petrol is near to that of Chilbolton, highlighting the contributions from leaded petrol at the flying club [31]. Pontardawe Brecon Road is similarly nearby, however uncertainties regarding the measurements are slightly larger than for other sites, so there is a larger element of doubt. Additionally the background concentrations owing to diffuse emissions are very low because of the site's location out of town and with elevation about ground level, hence the high concentrations it witnesses will be emissions from the local industrial plant when the wind in the right direction. The observed values for steel production and manufacturing plants at Scunthorpe and Port Talbot show good agreement, with a mixture of steel production and metal refining sources and blast furnaces fueled by European coal and coke. Unlike the study of Resongles et al., there is little evidence for the residual influence of leaded petrol in urban areas in the data gathered by this study [3]. If there are any residual sources from leaded petrol, these are very small compared to other traffic-based sources of lead and likely due to residual lead being resuspended from soils. In any event, the total concentration of lead at traffic influenced locations is very low and only about 2–3% of the regulatory limit value.

4. Conclusions

A high throughput lead isotope ratio measurement has been developed using ICP–MS/MS. For the first time, lead isotope ratio values in PM_{10} have been produced on a nationwide basis in the UK, and this novel data will contribute significantly to the body of knowledge in this area. Over 200 PM_{10} samples from the UK Heavy Metals Network were analysed using the new method. Values for $^{207}Pb/^{206}Pb$ ranged from 0.864 to 0.910 with an average standard error of 0.68%, while $^{208}Pb/^{206}Pb$ values ranged from 2.08 to 2.187 with an average standard error of 0.84%. The calibration method developed, using NIST SRM981, gave sufficient precision to see variation in lead isotope ratios between sites and site types. All isotope ratios measured fall within literature values for other studies of airborne particulate matter and have comparable precision to other studies that used quadrupole ICP–MS.

With respect to site type groupings, although there was significant overlap between some site types, showing that a mixture of sources are contributing, the extremes were shown to be statistically significant. In terms of individual sites, many sites fit well with their respective classification, although some examples suggest that site type assignments may require review to better represent the pollution climate at each monitoring station. This information can be combined with total lead concentration information from the UK Heavy Metals Network to conclude as to the primary contributions to each site from lead in PM_{10}.

The isotopic signatures observed at industrial-based sites agree well in absolute terms with literature values for metal refining and steel working. Furthermore, the measurements observed at traffic sites agree well with literature values related to unleaded petrol. Both observations demonstrate that the local sources most prevalent at the sites in question agree with the site types allocated to them. However, there are a number of exceptions to this, where the source of the lead collected at the site is clearly different from the dominant metal(s) defining the site classification. The reasons for this have been explained, based on other sources of lead impacting on the site. Perhaps the most interesting example of this is Chilbolton, a rural background site, whose lead isotopic signature was close to that of leaded petrol, indicating the sampling of emissions from a local airfield where small aircraft may still use leaded petrol. This outlier also highlights that all other sites (with the exception of Pontardawe Brecon Road) have little or no residual influence from leaded petrol contrary to some literature reports.

This work has demonstrated the utility of ICP–MS/MS as a fit-for-purpose analytical method for the high throughput of a large number of samples in complex matrices. Although isotope ratio analysis is not currently required by legislation, this method could be used effectively for routine analysis in future to better understand subtleties in changing pollution climates, perform source identification assessment for sites sampling multiple sources, and locate monitoring stations to more effectively sample relevant local point sources. Investigation of other isotope ratios, such as nickel, may also be beneficial for particular point sources, for instance in the Swansea and Tawe Valleys. Following on from this high throughput ICP–MS/MS analysis, targeted MC-ICP–MS analysis with higher precision could be beneficial for higher resolution source identification in specific areas of interest.

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References

1. Noble, S.R.; Horstwood, M.S.A.; Davy, P.; Pashley, V.; Spiro, B.; Smith, S. Evolving Pb isotope signatures of London airborne particulate matter (PM10)—Constraints from on-filter and solution-mode MC-ICP-MS. *J. Environ. Monit.* **2008**, *10*, 830–836. [CrossRef]
2. Meng, Q.; Richmond-Bryant, J.; Davis, J.A.; Cohen, J.; Svendsgaard, D.; Brown, J.S.; Tuttle, L.; Hubbard, H.; Rice, J.; Vinikoor-Imler, L.; et al. Contribution of particle-size-fractionated airborne lead to blood lead during the national health and nutrition examination survey, 1999–2008. *Environ. Sci. Technol.* **2014**, *48*, 1263–1270. [CrossRef]
3. Resongles, E.; Dietze, V.; Green, D.C.; Harrison, R.M.; Ochoa-Gonzalez, R.; Tremper, A.H.; Weiss, D.J. Strong evidence for the continued contribution of lead deposited during the 20th century to the atmospheric environment in London of today. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2102791118. [CrossRef] [PubMed]
4. Laycock, A.; Chenery, S.; Marchant, E.; Crabbe, H.; Saei, A.; Ruadze, E.; Watts, M.; Leonardi, G.S.; Marczylo, T. The Use of Pb Isotope Ratios to Determine Environmental Sources of High Blood Pb Concentrations in Children: A Feasibility Study in Georgia. *Int. J. Environ. Res. Public Health* **2022**, *19*, 15007. [CrossRef] [PubMed]
5. Goddard, S.L.; Williams, K.R.; Robins, C.; Butterfield, D.M.; Brown, R.J.C. Concentration trends of metals in ambient air in the UK: A review. *Environ. Monit. Assess.* **2019**, *191*, 683. [CrossRef] [PubMed]
6. Brown, R.J.C.; Yardley, R.E.; Muhunthan, D.; Butterfield, D.M.; Williams, M.; Woods, P.T.; Brown, A.S.; Goddard, S.L. Twenty-five years of nationwide ambient metals measurement in the United Kingdom: Concentration levels and trends. *Environ. Monit. Assess.* **2007**, *142*, 127–140. [CrossRef] [PubMed]
7. DEFRA. Heavy Metals Network. UK AIR: Air Information Resource. Available online: https://uk-air.defra.gov.uk/networks/network-info?view=metals (accessed on 13 July 2023).
8. BEIS. National Atmospheric Emissions Inventory. Available online: https://naei.beis.gov.uk/ (accessed on 10 May 2024).
9. UK Government. The Air Quality Standards Regulations 2010. Available online: https://www.legislation.gov.uk/uksi/2010/1001/contents/made (accessed on 13 September 2023).
10. European Union. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. *Off. J. Eur. Union* **2008**, *L152*, 0001–0044.
11. DEFRA. Site Environment Types. UK AIR: Air Information Resource. Available online: https://uk-air.defra.gov.uk/networks/site-types (accessed on 9 April 2024).
12. Goddard, S.L.; Williams, K.R.; Robins, C.; Brown, R.J.C. Determination of antimony and barium in UK air quality samples as indicators of non-exhaust traffic emissions. *Environ. Monit. Assess.* **2019**, *191*, 641. [CrossRef] [PubMed]
13. Monna, F.; Lancelot, J.; Croudace, I.W.; Cundy, A.B.; Lewis, J.T. Pb Isotopic Composition of Airborne Particulate Material from France and the Southern United Kingdom: Implications for Pb Pollution Sources in Urban Areas. *Environ. Sci. Technol.* **1997**, *31*, 2277–2286. [CrossRef]

14. Huston, D.L.; Champion, D.C. Applications of Lead Isotopes to Ore Geology, Metallogenesis and Exploration. In *Isotopes in Economic Geology, Metallogenesis and Exploration*; Springer: Cham, Switzerland, 2023; pp. 155–187. [CrossRef]
15. Dong, S.; Gonzalez, R.O.; Harrison, R.M.; Green, D.; North, R.; Fowler, G.; Weiss, D. Isotopic signatures suggest important contributions from recycled gasoline, road dust and non-exhaust traffic sources for copper, zinc and lead in PM10 in London, United Kingdom. *Atmos. Environ.* **2017**, *165*, 88–98. [CrossRef]
16. Tong, S.; Meija, J.; Zhou, L.; Methven, B.; Mester, Z.; Yang, L. High-Precision measurements of the isotopic composition of common lead using MC-ICPMS: Comparison of calibration strategies based on full gravimetric isotope mixture and regression models. *Anal. Chem.* **2019**, *91*, 4164–4171. [CrossRef] [PubMed]
17. Platzner, I.; Ehrlich, S.; Halicz, L. Isotope-ratio measurements of lead in NIST standard reference materials by multiple-collector inductively coupled plasma mass spectrometry. *Anal. Bioanal. Chem.* **2001**, *370*, 624–628. [CrossRef] [PubMed]
18. Komárek, M.; Ettler, V.; Chrastný, V.; Mihaljevič, M. Lead isotopes in environmental sciences: A review. *Environ. Int.* **2008**, *34*, 562–577. [CrossRef] [PubMed]
19. Xu, H.; Cao, J.; Ho, K.; Ding, H.; Han, Y.; Wang, G.; Chow, J.; Watson, J.; Khol, S.; Qiang, J.; et al. Lead concentrations in fine particulate matter after the phasing out of leaded gasoline in Xi'an, China. *Atmos. Environ.* **2012**, *46*, 217–224. [CrossRef]
20. Grotti, M.; Vecchio, M.A.; Gobbato, D.; Mataloni, M.; Ardini, F. Precise determination of 204 Pb-based isotopic ratios in environmental samples by quadrupole inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* **2023**, *38*, 1057–1064. [CrossRef]
21. Zheng, J.; Tan, M.; Shibata, Y.; Tanaka, A.; Li, Y.; Zhang, G.; Zhang, Y.; Shan, Z. Characteristics of lead isotope ratios and elemental concentrations in PM10 fraction of airborne particulate matter in Shanghai after the phase-out of leaded gasoline. *Atmos. Environ.* **2004**, *38*, 1191–1200. [CrossRef]
22. Usman, A.; Ander, E.L.; Bailey, E.H.; Nelms, S.; Pashley, V.; Young, S.D.; Chenery, S.R. Optimisation of a current generation ICP-QMS and benchmarking against MC-ICP-MS spectrometry for the determination of lead isotope ratios in environmental samples. *J. Anal. At. Spectrom.* **2018**, *33*, 2184–2194. [CrossRef]
23. DEFRA. DEFRA's UK-Air: Air Information Resource. Available online: https://uk-air.defra.gov.uk/ (accessed on 10 July 2023).
24. Butterfield, D.M.; Brown, R.J.C.; Brown, A.S. Seasonality of Heavy Metals Concentrations in Ambient Particulate Matter in the UK. *Atmosphere* **2024**, *15*, 636. [CrossRef]
25. *BS EN 14902:2005*; Ambient Air Quality. Standard Method for the Measurement of Pb, Cd, AS, and Ni in the PM 10 Fraction of Suspended Particulate Matter. European Committee for Standardization: Brussels, Belgium, 2005.
26. Goddard, S.; Brown, R.; Butterfield, D.; Robins, C.; Williams, K.; Lilley, A.; Bradshaw, C.; Sweeney, B.; Brown, L.; Sims, A. Annual Report for 2019 on the UK Heavy Metals Monitoring Network. 2019. Available online: https://uk-air.defra.gov.uk/library/reports?report_id=1042 (accessed on 1 June 2024).
27. DEFRA. UKNAEI Emissions Data Selector. Available online: https://naei.beis.gov.uk/data/data-selector?view=pms (accessed on 24 April 2023).
28. Weiss, D.J.; Kober, B.; Dolgopolova, A.; Gallagher, K.; Spiro, B.; Le Roux, G.; Mason, T.F.; Kylander, M.; Coles, B.J. Accurate and precise Pb isotope ratio measurements in environmental samples by MC-ICP-MS. *Int. J. Mass Spectrom.* **2004**, *232*, 205–215. [CrossRef]
29. NPL. XLGENLINE. Software. Available online: https://www.npl.co.uk/resources/software/xlgenline-and-xgenline (accessed on 11 August 2023).
30. Dang, D.H.; Schäfer, J.; Brach-Papa, C.; Lenoble, V.; Durrieu, G.; Dutruch, L.; Chiffoleau, J.-F.; Gonzalez, J.-L.; Blanc, G.; Mullot, J.-U.; et al. Evidencing the Impact of Coastal Contaminated Sediments on Mussels Through Pb Stable Isotopes Composition. *Environ. Sci. Technol.* **2015**, *49*, 11438–11448. [CrossRef] [PubMed]
31. Mills, A.; Peckham, S. Lead exposure from general aviation emissions in the UK: A review and call for action. *Public Health. Chall.* **2022**, *1*, e27. [CrossRef]